

Comment on 'Quantum Coherence between High Spin Superposition States of Single Molecule Magnet Ni_4 '

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Abstract

In a recent paper, <http://xxx.lanl.gov/abs/cond-mat/0405331> (Ref. 1), del Barco et al. reported experimental studies on a Ni_4 molecular system. They used an experimental method (combining microwave spectroscopy with high sensitivity magnetic measurements) that we have introduced before, <http://xxx.lanl.gov/abs/cond-mat/0404410> (see also Ref. 2 and 3). Among other things, our technique allows us to monitor spin-state populations in the presence of microwave magnetic fields. Absorption line-widths give rough 'upper bounds' on the decoherence rate similar to 'standard' high frequency electron paramagnetic resonance (HF-EPR) techniques. In the case of quasi continuous radiation our technique does **NOT** give directly the spin-lattice relaxation time T_1 . For measurements like those of del Barco et al., it simply gives access to the phonon-bottleneck time, a parameter that is many orders of magnitude longer than the spin-lattice relaxation time. Any conclusion concerning quantum coherence is preliminary.

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It is widely accepted that single-molecule magnets (SMMs) are interesting new model systems to study quantum dynamics. With respect to diluted paramagnetic ion systems, the extraordinary tools of organic and coordination chemistry allow the design of new (supra)molecular systems with promising properties [4]. SMMs straddle the interface between classical and quantum mechanical behavior because they also display quantum tunneling of magnetization [5, 6, 7, 8, 9, 10, 11, 12] and quantum phase interference [13, 14].

We reported recently [2, 3] a technique allowing us to monitor spin-state populations in the presence of microwave magnetic fields. Absorption line-widths give rough 'upper bounds' on the decoherence rate similar to 'standard' high frequency electron paramagnetic resonance (HF-EPR) studies [9, 15, 16]. The advantages of our technique with respect to pulsed EPR techniques involves the possibility to perform time-resolved experiments (below 1 ns) [17] on submicrometer sizes samples (about 1000 spins) [18] at low temperature (below 100 mK). Our first results on the V_{15} system open the way for time-resolved observations of quantum superposition of spin-up and spin-down states in SMMs. Other results obtained in similar systems but with large spins concern for example EPR measurements [9], resonant photon-assisted tunneling in a Fe_8 SMM [19] and non-resonant microwave absorption in a Mn_{12} SMM [20].

In a recent paper del Barco et al. reported experimental studies on a Ni_4 molecular system [1] similar to our study [2, 3]. However, they replaced the micro-SQUID by micro-Hall sensors. The latter has a lower sensitivity and it has not yet been shown that time-resolved experiments in the nanosecond range are possible. In the case of quasi continuous radiation our technique does **NOT** give directly the spin-lattice relaxation time T_1 . For measurements like those of del Barco et al. [1], it simply gives access to the phonon-bottleneck time [2, 3], a parameter that is many orders of magnitude longer than the spin-lattice relaxation time.

This comment recalls briefly the phonon-bottleneck effect that was first studied in diluted paramagnetic ion systems [21]. In the field of molecular systems, this effect was rediscovered [22, 24, 25] and it plays a certain role in all currently available molecular systems. The energy exchange between the spin system and the cryostat (heat bath) goes via the phonon lattice modes of the crystal. A phonon-bottleneck occurs as soon as the heat capacity of the phonons is much smaller than that of the spins. The energy Δ_H is transferred from the spins to only those phonon modes with the energy $h\nu = \Delta_H$ (within the resonance line-width). Because the number of such lattice modes is much smaller than the number of spins, the energy

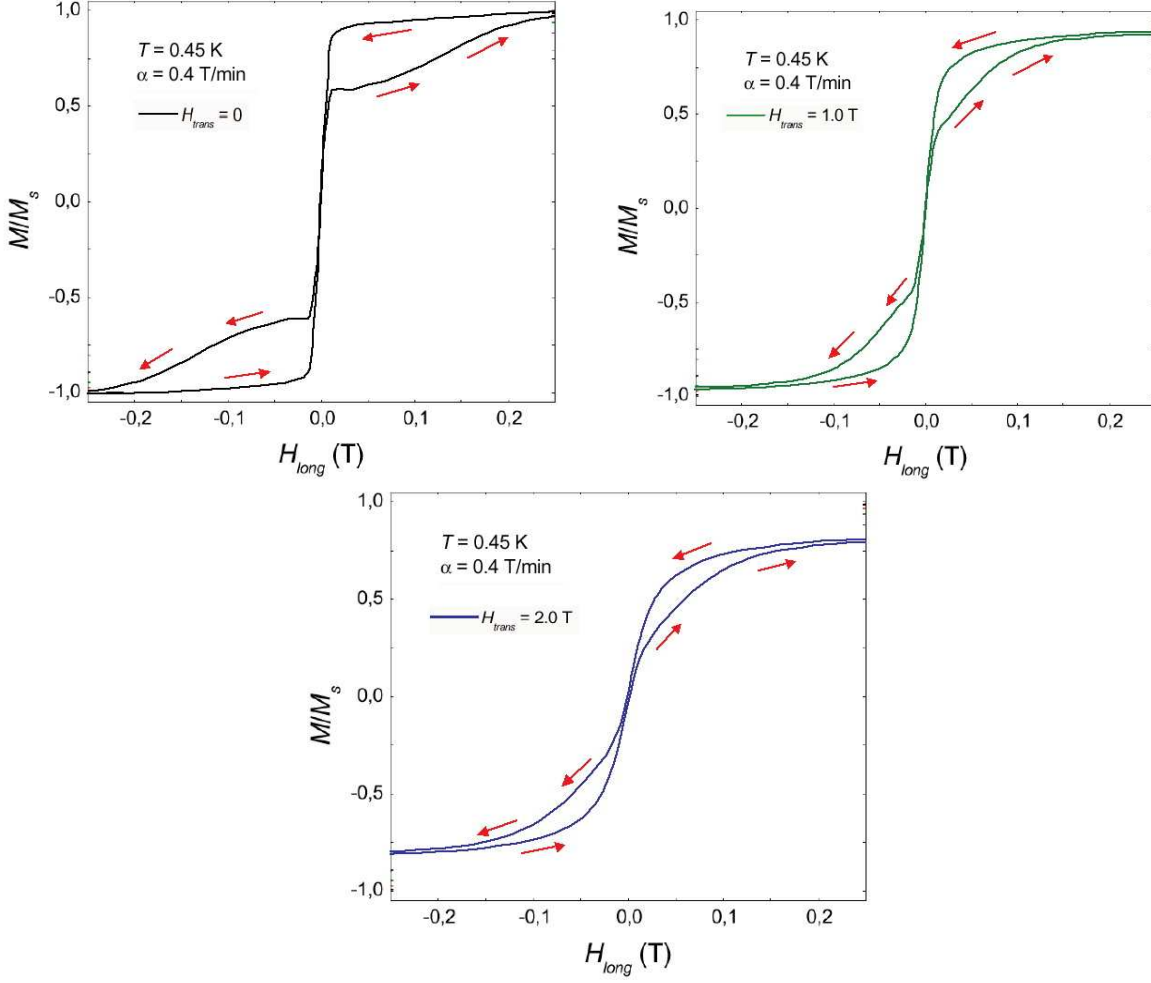


FIG. 1: (color) (a) Hysteresis loop measurements for a single crystal of Ni_4 at several transverse fields. The data were scanned from Fig. 1 in cond-mat/0405541. The back sweeps were obtained by a symmetry operation. Such loops are typical for a phonon-bottleneck effect [22, 24, 25]. Note that the field sweep rate is very small. The opening at this sweep rate corresponds to relaxation rates of a few tens of seconds, in agreement with Fig. 3 in Ref. 1.

transfer is very difficult, leading to a phenomenon known as the phonon-bottleneck [21].

The phonon-bottleneck time τ_{ph} depends on many experimental conditions: spin value, magnetic anisotropy of the spins, temperature, applied field, crystal size and shape, thermalization, sample holder, etc. Generally, for molecular systems below a few kelvin and for fields larger than a few tens of mT, τ_{ph} ranges from a few seconds to 1000 s [23]. The temperature dependence of τ_{ph} does not follow an Arrhenius law [22, 23].

The relaxation rates reported by del Barco et al. [1] on a Ni_4 molecular system are

typical for a phonon-bottleneck and had been measured by micro-SQUID measurements on the same system (unpublished, see also Fig.1). Each pulse of microwaves excites spins. It will take then a time τ_{ph} in order to transfer the energy from the spin system to the cryostat (heat bath). This heat transfer is 'slowly' because of the small heat capacity. The relaxation times are therefore not remarkably long and the increase from 8 to 20 s as the field increases is **not** contrary to general ideas that the relaxation time should decrease with frequency. In the phonon-bottleneck regime, such an increase is expected until the field reaches an energy splitting of a few kelvin. More details have been presented (Ref. 3) and will be published elsewhere.

Finally, we mention that this system does not block at zero field because of fast tunnel dynamics (even without transverse field). Below about 0.3 K, the system orders because of a small antiferromagnetic intermolecular exchange coupling. Both the conclusion that $\tau_2 \sim \tau_\phi$ and all statements concerning the observation of quantum coherence are not yet demonstrated. The RF-power estimations in Ref. 1 should take into account the phonon-bottleneck effect.

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- [2] W. Wernsdorfer, A. Müller, D. Mailly, and B. Barbara, <http://xxx.lanl.gov/abs/cond-mat/0404410>. In publication in Europhysics Letters, Vol. 66, N. 6, (15 June 2004).
- [3] The experiments like in Ref. 2 were proposed by B. Barbara in 1996 in analogy to results of superconducting devices (see Nakamura, Chen, Tsai, PRL, vol 79, 2328, (1997) and references therein). At a meeting in London in May 2002, the NYU group (A. Kent) presented the plan to do experiments using a high frequency network analyzer whereas the Grenoble group stated that they already have started such experiments (Thesis of C. Thirion, post-doc L. Sorace). At a meeting in London in May 2003, the Grenoble group presented three experiments: (i) the results of Ref. 2; (ii) results on doped Fe₆ wheels (see the web sites below); (iii) photon assisted tunneling in Fe₈ using circular polarized microwaves. All three results were discussed in detail during several hours. After several questions the present author explained in detail why the measurements in (ii) give directly a T_1 (spin-lattice relaxation time) whereas in (i) and experimental conditions like in Ref. 1 only the phonon-bottleneck time τ_{ph} . At that time, the high frequency network analyzer was not yet delivered to the NYU group (they received it in fall 2003). These results (i-iii) have been presented at many conference and network meetings during 2003. Some of the authors in Ref. 1 have been attending. More information can be found at: http://142.103.234.46:10000/CONFERENCES/QMLS_1/get_file.cgi?year=2003&month=4&day=16&eid=18, http://research.yale.edu/boulder/Boulder-2003/list_wernsdorfer.html, <http://www.lkb.ens.fr/recherche/qedcav/houches/Wernsdorfer.htm>
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